



Simplified Laboratory Runoff Procedure (SLRP): Procedure and Application

By Richard A. Price and John G. Skogerboe

PURPOSE: The Simplified Laboratory Runoff Procedure (SLRP) was developed to provide a faster, less expensive approach to evaluate surface runoff water quality from dredged material placed in an upland environment. SLRP is available as a tool for screening dredged material to estimate potential water quality problems and the need for more quantitative testing using the Rainfall Simulator/Lysimeter System (RSLS) and/or management activities. Previous Environmental Effects of Dredging Programs (EEDP) technical notes (Price, Skogerboe, and Lee 1998; Price 1999) describe the development and an example application of SLRP. The purpose of this technical note is to describe the SLRP chemical extraction procedures and application of results. Additional technical notes providing interpretive guidance and procedural updates will be provided at a later date. Both the RSLS and SLRP procedures will be included in the "Upland Testing Manual," currently in preparation.

BACKGROUND:

The Surface Runoff Water Quality Protocol: The surface runoff water quality component of the Decision-Making Framework (DMF) for the management of dredged material (Lee et al. 1991, U.S. Army Corps of Engineers/U.S. Environmental Protection agency (USACE/EPA) 1992) evaluates the potential water quality problems that may result from discharges of storm water from contaminated dredged material placed in upland environments. Water leaving an upland confined disposal facility (CDF) must receive Section 401 water quality certification by passing required standards based on potential for environmental impact. When dredged material is initially placed in a CDF, contaminant movement from the wet, unoxidized material will be mainly associated with suspended solids and is addressed by the effluent assessment protocol (USEPA/USACE 1998). During effluent discharge, the erosive effects of rainfall on exposed sediment may increase suspended sediment in the effluent discharge. As the material slowly dries and oxidizes, suspended solids concentrations normally begin to decrease while contaminants such as heavy metals may become more soluble. The Engineer Research and Development Center (ERDC) rainfall simulator lysimeter system (RSLS) predicts these effects so that restrictions and/or treatments, such as controlling movement of suspended solids or providing adequate mixing zones, can be incorporated into the CDF design.

The testing protocol for surface runoff water quality using the RSLS has been applied to dredged material from a number of locations including Indiana Harbor (Environmental Laboratory 1987), Black Rock Harbor (Skogerboe et al. 1987), New Bedford Harbor (Skogerboe, Price, and Brandon 1988), Oakland Harbor (Lee et al. 1992a, 1992b, 1993a, 1993b), and others. Contaminants have included heavy metals, PAHs, PCBs, pesticides, organotins, and dioxins. Although the RSLS is a very effective tool for predicting surface runoff water quality from upland CDFs, the procedure is expensive, time-consuming, and can only be conducted at ERDC. A need for a faster, less expensive screening tool for surface water quality concerns prompted the development of a simple laboratory

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procedure that could be performed by any qualified laboratory with widely available equipment. SLRP was designed to provide a less expensive, rapid response screening evaluation of surface runoff water quality from upland CDFs.

Method Development: A number of sediment drying and oxidation procedures were evaluated on Indiana Harbor sediment and compared to RSLs tests conducted using the same material (Environmental Laboratory 1987). A procedure using oven drying and hydrogen peroxide was selected as the best sediment treatment to simulate the long-term effects of drying and oxidation. The hydrogen peroxide test was originally developed as a test to determine potential soil acidity and lime requirements on mine spoils containing high levels of iron pyrite (FeS_2) or other sulfides (Barnhisel 1976). Exposing mine spoils to air results in the formation of H_2SO_4 and $\text{Fe}(\text{OH})_3$ and subsequent decrease in pH. Many marine sediments also contain high levels of sulfides that contribute to the same results, as oxidation occurs over time. The purpose of the hydrogen peroxide is to oxidize sediment in a matter of minutes or hours, when natural oxidation might require months or years. Reduction in pH and organic matter content may change the contaminant concentrations in surface runoff water. The effects can include significant increases in some dissolved heavy metal concentrations, no effect on other heavy metals, and volatilization and degradation of organic compounds. The SLRP was applied to San Francisco Bay and Black Rock Harbor sediments and compared to the RSLs results (Skogerboe 1995, Price et al. 1998). The results from these two sediments demonstrated the value of the SLRP as a screening procedure to determine the need for the more expensive RSLs procedure. Skogerboe (1995) began developing regression equations relating the SLRP results to the RSLs procedure results as a function of percent sand and total organic carbon (TOC) of the dredged material. The results of this work will improve the confidence of the SLRP and will be presented in additional technical notes.

Assumptions: Heavy rainfall on a CDF can dislodge sediment particles and contribute to high suspended solids concentrations in the resulting surface water. Depending on CDF management activities, this water may or may not be discharged from the CDF. If discharge is necessary, adjusting retention times to allow for settling can control suspended solids. However, soluble contaminants may still be at elevated levels in the surface water column and must be addressed. The surface runoff water quality assessment assumes either of two worse-case scenarios in determining potential water quality problems in the upland placement of dredged material. The procedure evaluates the surface water generated on the CDF as a result of rainfall. The sediment is evaluated under wet, anaerobic conditions where consolidation is at a minimum as interstitial water is removed. At this stage, suspended solids in rainfall-generated surface water within the CDF are possible within the range of 500 to 50,000 mg l⁻¹. The second, opposite worse-case scenario is that of complete dryness with no vegetative cover. Suspended solids in this stage may range from 50 to 5,000 mg l⁻¹. Suspended solids in runoff from previous RSLs rainfall events are shown in Table 1. Data shown are the mean of three consecutive events over a three-day period. In both scenarios, rainfall events are considered heavy (5.08 cm/h⁻¹ for 30 min), resulting in high displacement of soil particles and discharge of suspended solids is considered unrestricted. Management activities, particularly during filling and release of effluent, would not allow excessive suspended solids concentrations such as these and release of contaminants bound to suspended solids would be minimized. However, soluble contaminants could still be released even after suspended solids are reduced. During rainfall events, surface water in the CDF could contain high suspended solids

Table 1
Mean Suspended Solids Concentrations
from Other Sediments Evaluated Using the
RSLS, mg l⁻¹

Sediment	SS, Wet	SS, Dry
Indiana Harbor	6600	56
Blackrock Harbor	10326	167
Everett Harbor	6900	1000
New Bedford	7730	268
Oakland Inner	4447	1686
Oakland Upper	9140	970
Pinole Shoal	1500	618
West Richmond	3290	2340
Santa Fe Channel	6240	2130

concentrations and, particularly on aerobic dredged material, soluble contaminants. Even if the rainfall-generated surface water is restricted from discharge until suspended solids settle out, soluble contaminants would still be present in the ponded water. This is why SLRP evaluates surface runoff at elevated suspended solids concentrations. The SLRP is a screening tool to eliminate sediments from further evaluation for runoff water quality evaluations. The SLRP is not field-validated at this time and results indicating failure of water quality criteria may require reevaluation using the RSLS procedure or selection of CDF management activities to control runoff. However, discharge decisions based on the SLRP alone may result in inappropriate runoff management strategies or engineering controls.

METHOD:

Apparatus:

1. Centrifuge with centrifuge head for 500-ml capacity bottles.
2. 500-ml polycarbonate centrifuge bottles with teflon caps.
3. Horizontal mechanical shaker.
4. Millipore filter apparatus.
5. 0.45- μ m membrane filters.
6. 4-liter, narrow mouth clear glass bottles with teflon caps.

Reagents:

1. 30% hydrogen peroxide.
2. Concentrated nitric acid.
3. Concentrated sulfuric acid.

Sediment Collection and Preparation: Sediment core or grab samples are normally collected from the proposed dredging site for evaluation of various contaminant pathways. These may be composited into one bulk sediment or composited according to horizontal and/or vertical position. The SLRP procedure must be conducted on each composite considered for separate upland placement. No more than 22 L and a minimum 13.2-L volume of each composite to be tested is required. The sediment should be stored in a sealed polyurethane bucket at 4 °C until ready to conduct the SLRP procedure. Prior to removing sediment from the bucket, it should be thoroughly mixed using an electric mixer. Sufficient samples to conduct the SLRP evaluation can then be removed from the container.

Sediment Characterization:

Sediment Moisture: Three replicate samples (1-2 g) of wet sediment are placed in pre-weighed aluminum pans and oven-dried at 95 °C for 48 hr. The pans are then removed and reweighed to determine percent water on a dry weight basis using the formula $((\text{wet weight} - \text{dry weight}) / \text{dry weight}) \times 100$.

Sediment pH: Sediment pH is determined on three replicates using a 1:2 sediment to water ratio according to the procedures described in Folsom, Lee, and Bates (1981). Ten grams (oven-dry weight equivalent) of sediment are weighed into a tall 50-ml Pyrex glass beaker. Twenty milliliters of distilled or reverse osmosis (RO) water are added and the mixture is stirred with a polyethylene rod until all particles are saturated. The mixture is stirred with a magnetic stirrer for 1 min every 15 min for 45 min. After 45 min, the pH electrode is placed into the solution above the surface of the sediment and the pH is read on a pH meter.

Electrical Conductivity/Salinity: Electrical conductivity (EC) is determined on three saturated extracts of sediment using the method of Rhoades (1982). The extracts were measured on a YSI model 32 conductance meter to determine EC in mmhos cm^{-1} . Salinity is measured on the extracts using a model 10419 hand refractometer (American Optical, Buffalo, NY) and is reported in parts per thousand.

Total Organic Carbon: TOC is obtained using USEPA Method 9060 in SW-846 (USEPA 1986). Results are used to develop regression equations (Skogerboe 1995).

Particle Size Analysis: Particle size is determined using the method of Day (1956) as modified by Patrick (1958). This hydrometer method defines sand within a range of 0.05 to 2 mm. Results are used in the development of regression equations (Skogerboe 1995).

Preparation of Simulated Runoff Samples: The SLRP requires the preparation of simulated runoff water using wet, unoxidized and dry, oxidized sediment in sediment:water ratios corresponding to the suspended solids concentrations shown in Table 2. Each ratio for the wet and dry procedure should be replicated three times. For purposes of describing runoff water quality from CDFs, total contaminants refers to unfiltered samples and dissolved refers to filtered samples.

Table 2
Target Suspended Solids and Required Sediment for Simulated Runoff Samples from Wet Sediment

Sediment : Water Ratio	Suspended Solids, mg l ⁻¹	G ¹ Sediment / 2.5 Liters
1:2,000	500	1.25
1:200	5,000	12.5
1:20	50,000	125

¹ Oven-dry weight equivalent of wet sediment.

Wet Sediment Evaluation: The wet sediment evaluation begins with the placement of replicate wet sediment samples into three 4-L glass bottles using the oven-dry weight equivalents shown in Table 2. Volume of sample is dependent on the required chemical analysis. Typically, 2.5 L is sufficient to analyze metals and one class of organics. The volume required by the analytical laboratory should first be determined and the necessary volume required can then be generated. Deionized water is added to bring the total sample volume to 2.5 L (Figure 1). The containers are placed on a mechanical shaker and agitated for 1 hr to ensure complete suspension of sediment and sediment-to-water contact. Half the sample is placed into appropriate containers for contaminants of concern. The other half of the sample is centrifuged at 7,000 rpm's (8288 x g) and 15 °C for 10 min and then filtered through a 0.45-µm membrane or a 0.7-µm glass fiber filter as applicable to determine soluble contaminants. Filtered samples should be preserved according to specific requirements for each contaminant according to USEPA (1986). Typically, samples for metals analysis are preserved with concentrated nitric acid (HNO₃) to a pH level less than 2.0 and organic contaminants with concentrated sulfuric acid to pH levels less than 2.0. Samples are analyzed for total and soluble contaminants according to USEPA (1986) procedures.

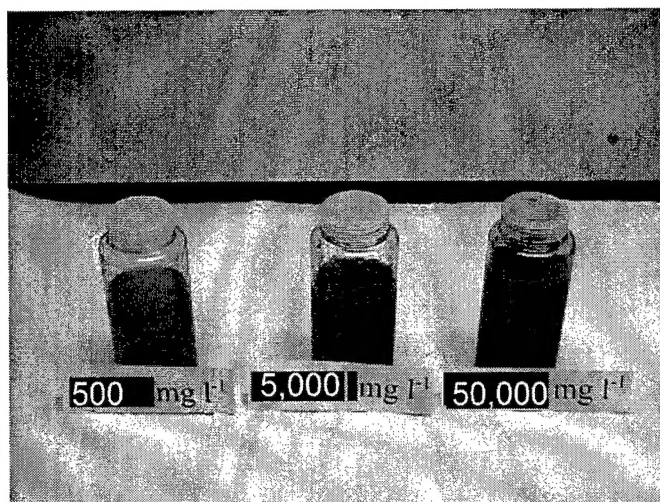


Figure 1. Wet sediment is mixed with water at the appropriate ratios

Dry Sediment Evaluation: The purpose of the dry portion of the SLRP is to predict the long-term effects of drying and oxidation of dredged material on movement of contaminants from an

upland CDF. Three replicates of wet, unoxidized sediment are collected from the bucket and placed in a drying oven at 90 °C for 48 hr. After drying is complete, 30-percent hydrogen peroxide (H_2O_2) is added to rapidly oxidize the sediment, simulating long-term exposure to drying and exposure to oxygen. A pretest is necessary to determine the amount of H_2O_2 necessary to fully oxidize the sediment. Ten grams of dried sediment is placed in a 4-L glass jar and 30-percent H_2O_2 is slowly and incrementally added each time, observing for an effervescent reaction (Figure 2). When the oxidation process is complete as indicated by lack of reaction, the amount of H_2O_2 used is recorded and the resulting H_2O_2 per gram of sediment is used in the SLRP procedure. The oven-dried sediment is oxidized with the volume of 30-percent H_2O_2 determined in the pretest and then mixed with RO water to the sediment:water ratios indicated in Table 3. The samples are shaken for 1 hr as described above and half of the samples are immediately placed in the appropriate sample containers. The remaining halves are then centrifuged and filtered as described for the wet sediment. Samples for both the wet and dry sediment are then analyzed for the contaminants of concern according to the methods described by USEPA (1986).

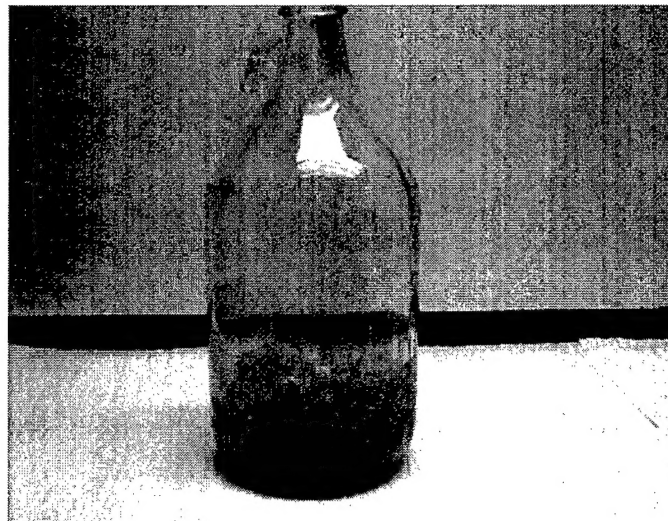


Figure 2. Oven-dried sediment is oxidized with hydrogen peroxide prior to dilution with water

Table 3

Target Suspended Solids and Required Sediment for Simulated Runoff Samples from Dry Sediment

Sediment : Water Ratio	Suspended Solids, mg/l ¹	G ¹ Sediment / 2.5 Liters
1:20,000	50	0.125
1:2,000	5,00	1.25
1:200	5,000	12.5

¹ Oven-dry weight equivalent of wet sediment.

APPLICATION AND INTERPRETATION OF RESULTS: The SLRP evaluates water quality using a range of expected suspended solids concentrations in the simulated runoff water. These ranges reflect the range of suspended solids concentrations measured in previous laboratory RSLs tests as indicated in Table 1. It would be expected that the suspended solids concentrations in rainfall-generated surface water within the CDF would be in the range of $5,000 \text{ mg/L}^{-1}$ during the initial wet stage with most dredged material. Once the material dries and forms a surface crust, suspended solids should fall to within the range of 500 mg/L^{-1} . The SLRP addresses concentrations on an order of magnitude above and below these concentrations. The chemical data obtained from the SLRP (three replicates at each suspended solids concentration) can be input into SigmaPlot® (or another statistical package) and regression lines can be plotted for total and dissolved contaminants from wet and dry sediment conditions. This gives an indication of contaminant concentrations in relation to suspended solids concentrations. In most cases, only the dissolved constituents are compared to water quality standards for the location of concern. In the absence of state or local standards, it is assumed that EPA criteria for the protection of aquatic life (USEPA 1987) would apply. Soluble contaminant concentrations that exceed the standards or criteria, after consideration of initial mixing, are reasons for concern. A decision must then be made to either conduct quantitative testing using the RSLs procedure or design engineering controls based on the screening level results of the SLRP. Engineering controls may include treating surface runoff water or restricting runoff discharges.

An example of how SLRP data are used to determine potential water quality problems is shown in Figures 3 and 4. Analytical results from an SLRP procedure for zinc (Figure 3) show that (1) solubility of zinc was not increased as a result of drying and oxidation, and (2) soluble zinc in runoff from both the wet (■) and dry (▼) sediment would be below the state saltwater standard (◆) that applied. Results for copper (Figure 4) indicate (1) increased solubility after drying and oxidation, and (2) failure of the saltwater standard from the dry sediment near the lowest suspended solids concentration tested. The dissolved copper in runoff from the dried sediment raises a red flag. The RSLs procedure would be required if excessive copper poses an unacceptable environment risk.

SUMMARY AND COMMENTS: The SLRP is a quick, simple screening tool designed primarily to eliminate sediments from further consideration for surface runoff water quality evaluations. It was designed primarily for metals but can be used to screen sediments for organic contaminants in runoff. Failure of the SLRP invokes the quantification of runoff water quality with the ERDC RSLs. At present, the SLRP is not a stand-alone procedure and should not be used to make engineering estimates or to design control measures on critical issues. The SLRP will be field-validated under the Dredging Operations and Environmental Research program and further refined as it is applied to additional sediments. Prediction equations have been developed for some metals by comparing SLRP results and the results of the RSLs procedure as a function of particle size and TOC (Skogerboe 1995). Entering the SLRP results into these equations provides more confidence in using the SLRP results as a predictive tool. To date, insufficient RSLs and SLRP data are available for organic contaminants, as most organics have been shown to be poorly soluble in runoff water. Technical notes will follow that include the prediction equations developed to date and additional interpretive guidance. As this research work unit continues under the DOER Program, additional updates to the SLRP procedure will be provided as necessary to assure the availability of the most up-to-date procedures.

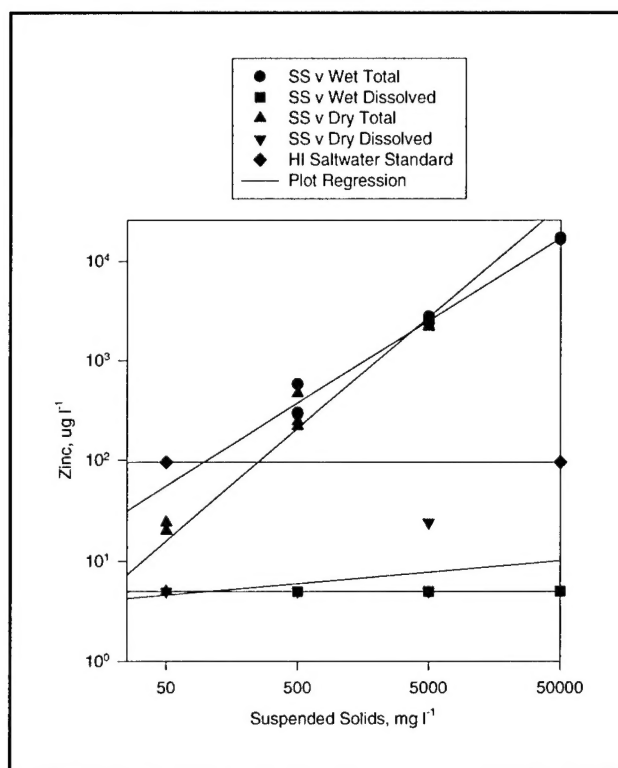


Figure 3. Zinc in SLRP runoff samples

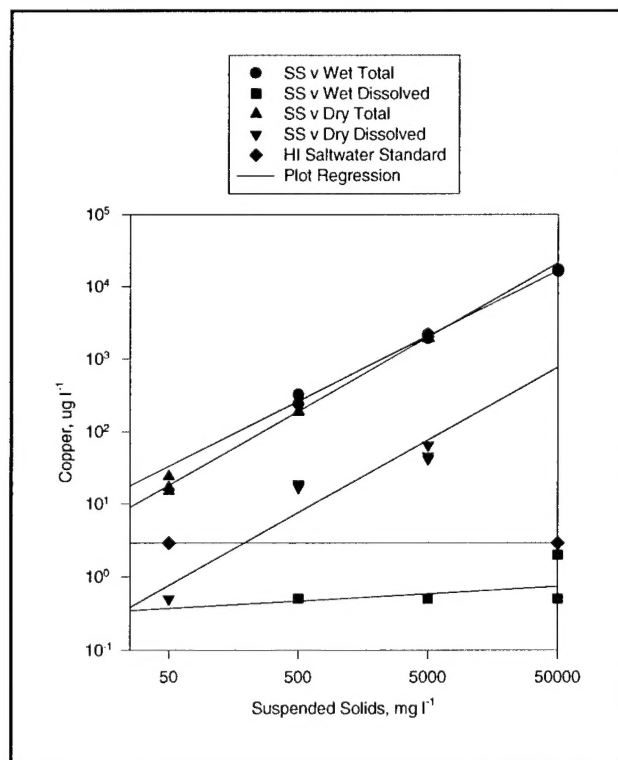


Figure 4. Copper in SLRP runoff samples

POINTS OF CONTACT: For additional information contact one of the authors, Mr. Richard A. Price, (601) 634-3636, *price1@ex1.wes.army.mil*, Mr. John G. Skogerboe, (972) 436-2215, or the manager of the Environmental Effects of Dredging Programs, Dr. Robert M. Engler, (601) 634-3624, *englerr@ex1.wes.army.mil*.

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